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A Study of Color Change in Stored Apple Juice Concentrates[a]

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Full-flavor 68°-69° Brix apple juice concentrates were stored at 5°, 25°, and 37.8° C. (41°, 77°, and 100° F.). Measurements of color density were made at frequent intervals for periods up to a year and plotted graphically. The effects of ion-exchange and various other treatments of the juices before concentration upon the rate of darkening of the concentrate were demonstrated.

A problem of some importance in the marketing of fruit juice concentrates for beverage purposes is their lack of color and flavor stability on unrefrigerated storage. Concentrates containing more than 65% total solids are normally stable against fermentation at any temperature; but when stored at elevated temperatures, those of some fruits turn dark and develop off-flavors. If means could be found to reduce these changes, such products could be stored under temperature conditions which are not now satisfactory for products of this type. This would result in considerable saving in warehousing and marketing costs. It would also increase the feasibility of their use in rations for the armed forces, where elevated storage temperatures are often encountered.

Darkening or browning is also a problem in the utilization of fruit concentrates for non-beverage purposes; for example, in the manufacture of candies, confectionery gels (for use with bakery products) and apple-fruit jellies. In the latter case, a dark-colored apple concentrate tends to mask the bright color of the other fruit.

A method for preparing a high density, full-flavor apple juice concentrate has been developed by Eskew, Redfield, and Phillips of the Eastern Utilization Research Branch *(3)*, based on the recovery and concentration of the volatile flavors by Milleville and Eskew *(5)*, these flavors being reincorporated after the remaining juice has been depectinized and concentrated to 71° Brix. The resulting 68.5° Brix concentrate may be reconstituted by the addition of 6 volumes of water, to give a 12.5° Brix full-flavor juice, substantially equal in quality to the fresh juice.

The concentrates described above do not have to be frozen. At 35° F. (1.7° C.) they may be stored for a year or more without serious loss of color or flavor. Recent modifications of the process have made it feasible to store these concentrates at normal room temperature also. However, at the higher temperatures which may sometimes be found in commercial storage, and which often prevail in military storage, serious darkening and deterioration of flavor may take place.

Color changes may be conveniently measured on small samples, but the measurement of flavor changes requires larger quantities of juice, and involves more complicated procedures. Therefore, the present study attempts only to follow changes in color during storage. Since the relations between color changes and flavor changes have not been definitely established, the latter will require a separate study.

EXPERIMENTAL PROCEDURE

The apple juice was prepared from a blend of varieties consisting of two parts of Jonathan and one part each of McIntosh, Northern Spy, and Stayman Winesap. Immediately after pressing, the juice was passed through an essence recovery apparatus *(3)* from which the volatile flavors were recovered in the form of an essence having 1/150 the volume of the original juice, and was simultaneously pasteurized by a 4-second heating at 101° C. (214° F.). The stripped juice was then clarified by adding Pectinol A,[c] allowed to stand overnight at room temperature, filtered, heated to 99° C. (210° F.) in less than 2 seconds to inactivate the enzyme, and cooled instantly by flashing into a vacuum. It was then run into 3-gallon enamel-lined tins and frozen. Cans of frozen juice were withdrawn and thawed when desired for experimental work. The stripped juice had a Brix value of 18.3°. The pH was 3.35, the total titratable acidity 0.705% (calculated as malic acid), and the total nitrogen 6.9 mg. per 100 ml. (determined by micro-Kjeldahl method).

The juice was concentrated in a laboratory vacuum still consisting of a 500-ml. round-bottom flask, a Friedrichs condenser, and an ice-cooled suction-flask receiver connected to an aspirator. The distilling flask was heated gently in a water bath, the temperature of the distilling vapor being kept below 35° C. (95° F.). When the contents of the flask reached 71° Brix or slightly above, the distillation was stopped. The concentrate was mixed with the amount of apple essence that had been recovered from the juice used to make it, and the concentration adjusted to 68.5° Brix + 0.5°. All Brix measurements were made on an Abbé refractometer, using the sugar scale.

Color was evaluated by means of a Klett-Summerson filter photometer, using standardized test tubes. The tubes were filled to the 10-ml. mark and closed with cork stoppers. There was approximately 5 ml. of air space between the surface of the liquid and the cork. The filter used in the photometer was prepared by combining a blue glass with an orange glass. This filter gave a single, rather narrow peak of transmittance in the yellow range with the maximum point at 565 millimicrons. Scale reading, proportional to absorbance, or optical density, was used as an index of color or darkening.

Three storage temperatures were chosen. The first group of samples was stored in a laboratory refrigerator at 5° C. ± 2° (41° F.). The second group was stored in the dark at room temperature at 25° C. ± 5° (77° F.). The third group was stored in an incubator at 37.8° C. ± 0.2° (100° F.). These temperatures were designated as low, medium, and high, respectively. The low and medium temperatures represent the usual conditions for storing fruit juice concentrates in commerce. The high temperature is that commonly used, for example, by the Quartermaster Corps, as an extreme test for storage stability.

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[c] The mention of commercial products is not to be construed as an endorsement by the U. S. Department of Agriculture over other products not mentioned.

Color measurements were made on each sample at the time of preparation, and at frequent intervals thereafter (usually 5 times each week) for periods up to a maximum of a year. The tubes of the low temperature series were removed from the refrigerator and allowed to warm up to a temperature above the dew point before making the readings. Each tube was carefully dried before placing in the colorimeter. In order to make sure that these short periods of warming up did not materially affect the rate of color change, a few checks were made by removing some tubes for reading only once a week. Readings on these samples did not differ significantly from those made on duplicate samples which were read more frequently.

Readings with the yellow filter were discontinued when the values reached 900 on the colorimeter scale. In some cases, however, further readings were made beyond this point by substituting a standard red filter (No. 66), which gave lower values of absorbance.

RESULTS

Figures 1 and 2 demonstrate the rate of darkening of a typical apple juice concentrate at three temperatures. Figure 1 is a magnified section of Figure 2, covering the first 45 days of storage. The rapid increase at medium and high temperature during the first few days of storage was obtained in every case with concentrates from untreated juice. At 25° C. the color reading rose sharply after 1 or 2 days and reached a peak at 5 to 7 days, then fell slightly and leveled off. At 37.8° C. the rise began immediately, and a peak was reached in 1 or 2 days, followed by a sharp drop. The peak at the high temperature may be lower in magnitude than that at the medium temperature, but sometimes reaches almost the same value. At 5° C. the curve started out level, or with a slight drop.

Visual observation showed no turbidity during the period in which these peaks appeared, and the change in color was easily detectable by the eye. A sample of concentrate from untreated juice, stored at 25° C., which reached a color peak at 7 days' storage, was examined under a light-scattering photometer and showed only a slight increase in light-scattering effect. Filtration through a fine sintered glass filter caused no decrease in color reading. Therefore, it may be assumed that the peaks represent an actual increase in color, rather than an increase in turbidity.

These preliminary peaks might be explained by the existence of a relatively rapid oxidation, independent of the overall browning reaction. With concentrates containing ascorbic acid, they are absent or considerably diminished.

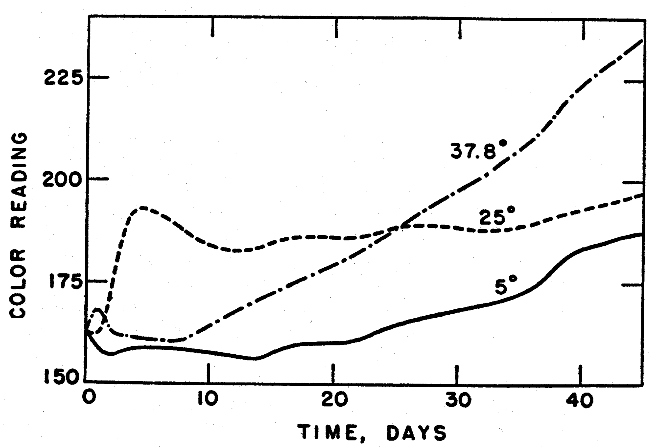

Figure 1. Color change in untreated apple juice concentrate.

Figure 2 shows the curves extended to cover a period of 9 months. The curves for the low and medium temperatures were close together and parallel from 1 to 3 months, after which they began to diverge, the low temperature curve leveling off and remaining practically flat for the rest of the period, while the medium temperature curve continued to rise at a practically constant rate. From 9 to 12 months, although not shown in the figure, both curves continued as approximately straight lines. The high temperature curve rises steadily after the first 10 days, the slope of the curve increasing in steps up to 3⅓ months. Beyond the latter point, the curve was practically straight. The maximum readable value of 900 was reached in 5½ months.

Effect of presence of essence. Since the reincorporation of volatile flavor concentrate (essence) was an integral part of these experiments, the question arose as to the possible effect of its presence upon the rate of darkening. Therefore, a sample of concentrate was prepared to one portion of which the usual amount of essence was added. The remaining portion was reduced to 68.5° Brix by the addition of water and stored without added essence. The rates of color change were not significantly different.

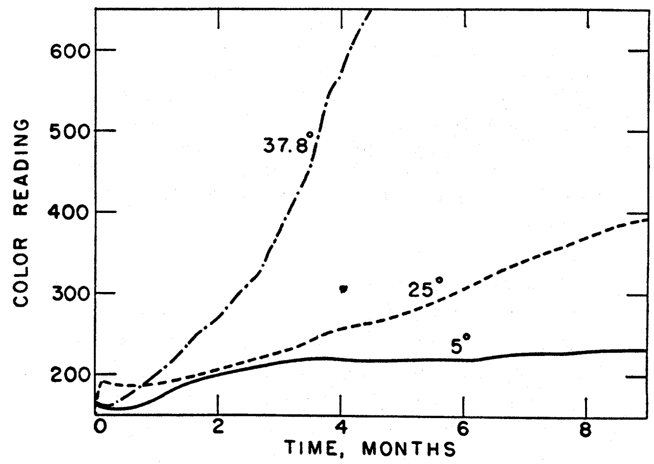

Figure 2. Color change in untreated apple juice concentrate.

Effect of light. A sample of concentrate was exposed to diffused daylight by placing near a north window of the laboratory. The rate of color change did not differ significantly from that of the same concentrate stored in the dark at the same temperature.

Effect of lack of air space. Three tubes were prepared by filling with concentrate to a level one-half inch from the top and filling the tube with melted paraffin wax in order to eliminate the head space. These tubes were stored at all three temperatures and compared with samples of the same concentrate prepared and stored in the usual manner. At low and medium temperatures the curves were identical for the first 5 months, after which they diverged somewhat. At the end of a year, the color reading of the sample in the tube without head space was 40 units lower at the low temperature and 95 units lower at the medium temperature. At the high temperature, the curves began to diverge at 1½ months, and the tube without head space required about 3 weeks longer to reach a reading of 900.

Effect of ascorbic acid. Ascorbic acid was added to a sample of the stripped juice at the rate of 0.5 g. per liter before concentrating. Comparison was made with a control sample prepared at the same time. The starting color for the treated concentrate was 151 as compared to 173 for the control. As noted above, the usual initial peaks were absent. In fact, the medium and high temperature samples showed a drop of 17 to 25 units in the first 2 days. The low temperature curve was almost flat up to 2½ months, after which it rose gradually and approached the curve for the control, merging with the latter at 11 months. The medium temperature curve, after an initial dip and recovery, rose only slightly up to 2 months, then more rapidly, crossing the control curve at 2½ months. At 5 months the curves recrossed, and from then on the ascorbic acid sample was appreciably lighter than the control. At the high temperature, the ascorbic acid sample darkened somewhat more rapidly than the control, perhaps as a result of the formation of colored products by reaction of the ascorbic acid itself.

Effect of decolorization with carbon. A sample of the stripped juice was stirred with decolorizing carbon (Darco G-60) at 70° C. (158° F.) for 20 minutes, then filtered and concentrated. The color change, shown in Figure 3, may be compared with that

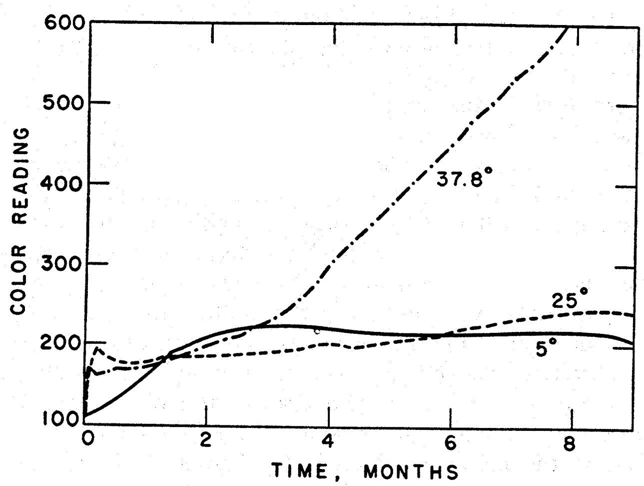

Figure 3. Color change in concentrate from apple juice treated with decolorizing carbon.

of the control, which is shown in Figure 2. The starting color of the treated concentrate was 109 as compared to 163 for the control. The medium and high temperature curves rose rapidly and then leveled off. The low temperature curve rose at a moderate constant rate, intersecting the other two curves at 1⅓ months. It continued to rise up to 3 months and then began a gradual decline. The medium temperature curve rose slowly in a straight line, crossing the low temperature curve at 5⅔ months. The high temperature curve rose more rapidly, but the slope was much less than that of the control.

Effect of bisulfite. A sample of freshly-prepared concentrate was treated with sodium metabisulfite in an amount equivalent to 200 p.p.m. of SO_2. The treated concentrate was stored without air space in test tubes sealed with paraffin. At the low temperature, the color decreased slowly, dropping 20 units in 6 months. At the medium temperature, it dropped 50 units in the first 1½ months and then remained practically constant up to 6 months. At the hgh temperature, it dropped over 50 units in the first 10 days, then began to rise, the slope of the curve increasing gradually. After 5 months the rate of increase was about the same as it would have been in an untreated sample. These data seem to indicate that sulfur dioxide reacts with certain pigments and color producing compounds in the concentrate, and that this reaction takes place more rapidly and reaches completion more quickly at the higher temperatures.

Effect of added amino-acids. The relationship between amino-compounds and browning is well recognized. The reactions between amino-acids and reducing sugars, in which melanoid pigments are produced, have been thoroughly investigated in model systems, and their relations to browning in many natural foods and processed food products have been studied. Apple concentrate contains small amounts of amino-acids, which probably play a part in the color changes noted above. It was therefore decided to test the effect on rate of darkening of adding small quantities of specific amino-compounds to the juice before concentration. Aspartic acid, glutamic acid and glutamine, which were all found to be present in the juice (at a level of about 5 to 15 mg. per liter), were chosen for this test.

Samples of stripped juice were treated by adding aspartic acid, glutamic acid and glutamine, respectively, at the rate of 20 mg. per liter, and were then concentrated in the usual manner. A sample of untreated juice was concentrated at the same time as a control. All samples were stored at the usual temperatures.

At the low temperature the color curve for the concentrate containing glutamine was essentially identical with that of the control. Those for aspartic and glutamic acid were slightly higher, the differential at the end of a year being 24 units for the former and 28 for the latter. At the medium temperature all treated samples darkened appreciably faster than the control, especially during the period between 2 and 8 months. Thereafter, the curves were essentially parallel. At the high temperature, the treated samples all darkened more rapidly than the control up to 3 months, and at about the same rate thereafter.

ION-EXCHANGE TREATMENT

Since amino-acids play a part in the darkening of apple concentrate, it should be possible, by reducing the amino-acid content of the juice, to reduce the rate of darkening. Challinor, Kieser and Pollard *(1)*, by means of a three-stage ion-exchange treatment, were able to reduce the nitrogen content of apple juice to the point where it would no longer support fermentation. Marshall and Walkin *(4)* produced a similar result by a single passage through a strongly acidic cation-exchange resin. This type of resin has been shown *(2)* to take up all amino-acids by reaction with the amino-group, whereas anion-exchange resins do not remove the basic amino-acids. Since cationic and anionic constituents were shown to be removed to a greater extent than the total nitrogen *(1)*, the estimation of total nitrogen may be used to indicate the degree of removal of amino-acids.

Marshall and Walkin found that ion-exchange treatment of fresh juice removed a large part of the volatile flavor. This involves no disadvantage when the treatment is applied to stripped juice, as in the present study.

Preliminary experiments were carried out by stirring stripped apple juice with varying amounts of several different cation-exchange resins. As a result of these tests, Zeo-Rex, a strongly acidic sulfonated phenolic resin, was chosen for the succeeding experiments. A 200-ml. bed of resin was prepared in a 1-inch column. Regeneration was carried out with 2% sulfuric acid.

Stripped apple juice was run through the column and the effluent collected in fractions. Each fraction of the first run was tested for pH, Brix, color and total nitrogen. The nitrogen content of the effluent began to increase at the same point at which the pH began to rise; consequently, the pH change was chosen as a guide for subsequent runs. All fractions showing the minimum pH were combined. The volume of this combined effluent varied from 1500 to 1800 ml. per run. The pH varied in different runs between 2.1 and 2.3 and the total nitrogen between 1.0 and 1.7 mg. per 100 ml., as compared to 6.9 for the stripped juice.

Samples of the effluent were restored to the original pH by the addition of NaOH solution, then concentrated, and the concentrate stored in the usual way. Figure 4 shows the rate of darkening for a typical sample. The starting color of the concentrate was 110 as compared to 163 for the control (Figures 1 and 2). At the low temperature the color was constant for 12 days, rose fairly rapidly to 1½ months, then slowly to 6½ months, and then remained nearly constant. From 6 months on the curve was practically identical with that of the control. At the medium temperature, after a rapid rise, the color was almost constant up to 2½ months and then rose gradually, remaining well below the control. After 11 months it was 80 points lower than the control. At the high temperature there was a rapid rise, a short dip, and a general rise. The rate of darkening was well below that of the control.

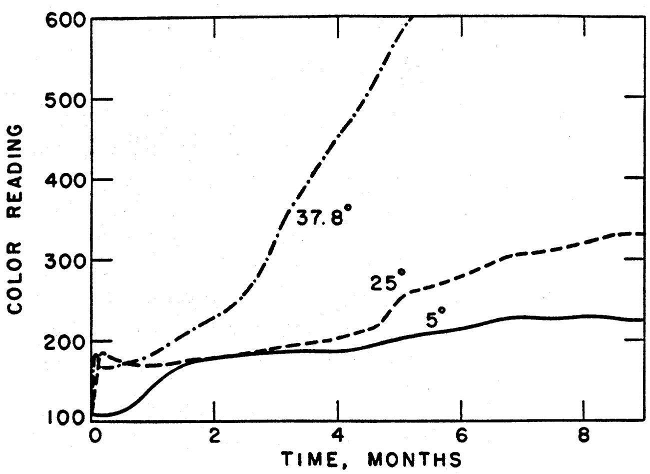

Figure 4. Color change in concentrate from apple juice treated with cation exchange resin.

Ion-exchange may be effectively combined with other treatments. When carbon-decolorized juice was passed through the cation-exchange column, it showed a marked decrease in rate of darkening at medium and high temperatures. An example of what may be accomplished by combined treatments is shown in Figure 5, which gives color curves for a concentrate prepared from stripped juice which had been treated with carbon, passed through the cation exchanger, and treated with ascorbic acid. Preliminary peaks are absent. At the low temperature, the curve is almost level for the entire period. At the medium temperature the rate of darkening is quite low. Even at the high temperature, the color reading is only 520 after 9 months' storage, whereas untreated concentrates would have long since passed the maximum readable value.

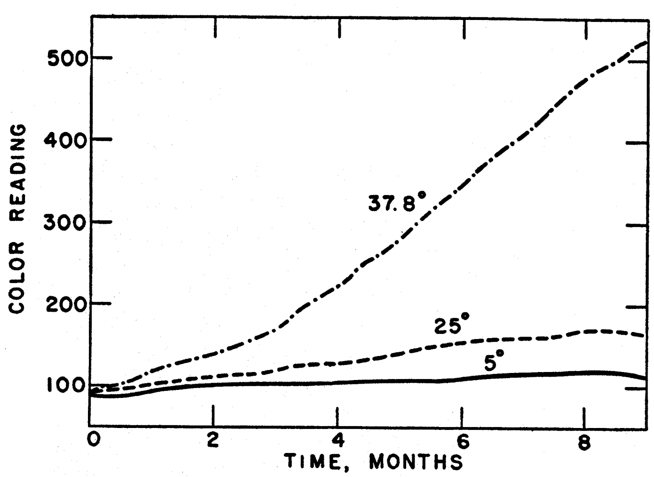

Figure 5. Color change in concentrate from decolorized apple juice treated with cation exchange resin and ascorbic acid.

Two-stage ion-exchange treatment. Samples of stripped juice were passed through the cation-exchange column in the manner described above, and the effluent was passed through a column containing Permutit S-2,[c] a strongly basic anion-exchange resin. The effluent had a nitrogen content of 0.62 mg. per 100 ml. and a titratable acidity of 0.013% as malic acid. The pH was approximately the same as that of the original stripped juice. This juice was of no value as a beverage, on account of its very low acid content. Therefore the acidity was restored by the addition of pure organic acid in an amount equivalent to the original acidity of the juice. The pH was then adjusted with sodium hydroxide, and the juice was concentrated. Three acids—malic, citric, and tartaric—were used for the acidification. At low and medium temperatures, these concentrates showed practically no darkening at all over a period of more than 6 months. At the high temperature the rate was still quite low, varying somewhat with the acid added, with tartaric the highest and citric the lowest. At the low temperature, tartaric acid began to crystallize out after 2 months' storage. It should be noted that citric acid alters the flavor of the juice considerably and tartaric acid to a lesser extent. These flavor changes are not in any sense deleterious. They are, in fact, preferred by some tasters.

Two-stage ion-exchange was the most effective treatment of all those tested in this study at low and medium temperatures. At the high temperature, carbon treatment plus single-stage ion-exchange gave the best results.

SUMMARY AND CONCLUSIONS

The darkening of full-flavor apple juice concentrate was studied at three temperatures, viz., 5°, 25°, and 37.8° C. (41°, 77°, and 100° F.). In general, the rate of darkening is a positive function of the temperature. Untreated concentrates undergo an immediate rapid rise in color at high and medium temperatures, followed by a short drop or a leveling off. The presence of essence does not appreciably affect the rate of darkening. Light does not increase the rate of darkening at room temperature. The elimination of air space results in less darkening from 3 months on at low and medium temperatures, and from 1½ months at high temperature. Ascorbic acid gives lighter concentrates at low temperature up to 11 months and at medium temperature from 5 months on. At the high temperature, ascorbic acid increases the rate of darkening. Concentrates from juices decolorized with carbon darken rapidly at first, but the overall rate is lower than for control samples. Bisulfiite causes a rapid lightening of color at high and medium temperatures, but at the high temperature, the effect is only temporary. The addition of aspartic acid, glutamic acid, or glutamine increases rate of darkening.

A single pass through a Zeo-Rex cation-exchange column reduces the total nitrogen content of stripped apple juice from 6.9 to 1.0 mg. per 100 ml. When the excess acidity is neutralized and the juice concentrated, the resulting concentrate shows a reduced darkening rate. Ion-exchange may be effectively combined with carbon treatment or ascorbic acid treatment to give concentrates of good color stability. Successive treatment with cation- and anion-exchange materials, followed by restoration of organic acid content and pH adjustment gives concentrates whose color remains almost constant at low and medium temperatures and shows a greatly reduced rate of darkening at high temperature. This treatment gives the best results of all those tried at low and medium temperatures.

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